Microstructural Improvement of NdFeB Magnetic Powders by the Zn Vapor Sorption Treatment

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The microstructural modification for NdFeB magnetic powders (MQP-B) after Zn vapor sorption has been investigated by transmission electron microscopy (TEM). It is found that a coating layer about 100 nm thick was formed on the surface of powder. Selected area electron diffraction (SAED) pattern and high resolution transmission electron microscopy (HRTEM) analyses show that the coating layer consists of condensed nano-scale crystallites of $Fe_{11}Zn_{40}$, $NdZn_5$ and Zn. After the temperature for Zn vapor sorption is raised to 648 K, a thin layer has been formed on boundaries of $Nd_2Fe_{14}B$ grains locally in the rim region of the powders. The morphology of the grain-boundary thin-layers is very similar to that in HDDR-NdFeB magnet powder after Zn vapor sorption treatment. Since the latter has a good thermal stability of magnetic property, the Zn vapor sorption treatment is expected to improve also the thermal stability of MQP-B magnet.

1. Introduction

Bonded magnets produced by dispersing NdFeB magnetic powders in polymeric binder are widely used in many electric and electronic apparatuses since they have significant advantages in terms of shaping and cost. However, NdFeB magnetic powders exhibit a poor corrosion resistance especially in hot humid environments.[1] The corrosion is thought to lead to deterioration of the magnetic properties, and then hinders wider applications of the magnets, such as components of motors in automobiles.[2]

To protect NdFeB magnets from the corrosion, coating with corrosion-resistance metals such as Ni, Al and Cu is often used. Recently, Zn has been applied as an effective coating for the purpose. Walton *et al.*[3] have pointed out that the Zn coating with the "Low Pressure Pack Sublimation process" is a cheap and effective coating technique for NdFeB magnets. Jakubowicz[4] has also reported that the electrodeposited Zn coating can protect against corrosion for nanocomposite NdFeB/α-Fe magnets. Machida *et al.*[5] developed a Zn vapor sorption treatment with a small amount of Zn. They have reported that bonded magnets with the Zn coated $Sm_2Fe_{17}N_x$ powders had a good thermal magnetic stability and a less reduction in the magnetic properties as well. In addition, the Zn vapor sorption treatment was applied to NdFeB magnetic powders. Similar effect on the thermal stability of magnetic properties could be obtained in the Zn coated NdFeB bonded magnets.[6] The improvements in the corrosion resistance and the thermal stability of magnetic properties are attributed to the changes in microstructure of the powder by the Zn vapor sorption treatment. In the present work, the modification in the microstructures of practical NdFeB powders by the treatment was investigated with TEM to discuss the ideal coating structure to obtain a good corrosion resistance.

2. Experiment

Commercial melt-spun NdFeB powders (MQP-B, Magnequench International, Inc.) were used as starting material for this study. The powders are sieved to get a particle size smaller than 150 μm. Zn coating was performed by a vapor sorption treatment[5] described as follows. The magnetic powders and Zn powders were sealed together with a suitable quantity of steel balls in a stainless steel capsule under a vacuum atmosphere. The capsule was then rotated at 623 or 648 K for 10.8 ks to prepare Zn coated NdFeB powders. The former treatment (623 K) was found to improve the magnetic stability: The magnetic flux loss after exposed in air at 397 K for about 1 Ms was less than 6%, while that without the treatment is about 8%.[6]

The microstructures of the Zn coated NdFeB powders were observed with a JEM-2000EX transmission electron microscope operating at an accelerating voltage of 200 kV. Specimens for TEM were prepared by the following method. The Zn coated NdFeB powders embedded in epoxy resin, were thinned to electron transparency using an Ar^+ ion mill (Gatan Model 691), following conventional grinding and dimpling.

3. Results and Discussion

3.1 Microstructure of MQP-B powders before Zn vapor sorption

Figure 1 shows a typical bright field image of a MQP-B powder. One can see that the powder was made of polygonal $Nd_2Fe_{14}B$ grains. By close analysis of the TEM image and diffraction pattern, it was confirmed that there is no other
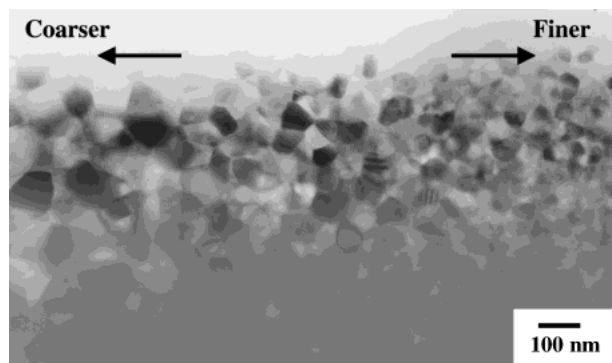
Fig. 1   Typical microstructure of a MQP-B powder before Zn vaper sorption treatment. The grain size of $Nd_2Fe_{14}B$ varies gradually.

phase at the grain boundaries. The $Nd_2Fe_{14}B$ grains have different sizes: the finer grains are about 30 nm in diameter and the coarser are about 100 nm varying gradually. Since the cooling rate is different in the melt-quenched ribbon between the wheel side and the free side, the grain size usually varies accordingly. The variation in grain size in the present powder is explained as the processing-induced feature.[7]

3.2   Microstructure of MQP-B powders after Zn vapor sorption at 623 K

After Zn vapor sorption, the modified microstructures of MQP-B powder were observed in several regions with different grain sizes as shown in Fig. 2. As is obviously seen in these images, a coating layer is formed on the surface of the powder, irrespective with the $Nd_2Fe_{14}B$ grains size. The layer consists of very small crystallites and has a uniform thickness about 100 nm.

A series of selected area electron diffraction (SAED) patterns Diff 1, Diff 2 and Diff 3 as shown in Fig. 3 were taken from the areas marked in the Fig. 2(b), respectively. Diff 1 taken from the coating layer shows a continual ring-pattern, while Diff 2 taken from the region including both of the coating layer and $Nd_2Fe_{14}B$ grains shows a mixture of ring and spot patterns. Diff 3 pattern was taken from the inner area in Fig. 2(b), and the pattern consists of the diffraction spots from the $Nd_2Fe_{14}B$ grains. It can be identified that the diffraction spots are from $Nd_2Fe_{14}B$ grains and the rings are from the coating layer. It should be noted that the $Nd_2Fe_{14}B$ grains in the inner region of the powder are not altered by the Zn vapor sorption.

It was found that a rather thick coating layer formed on a hydrogenation-decomposition-desorption-recombination (HDDR) NdFeB powders after the Zn vapor sorption treatment.[8] The layer on HDDR-NdFeB powders showed strong X-ray diffraction lines in the powder pattern, which was analyzed to contain $Fe_{11}Zn_{40}$ and $NdZn_5$. The coating layer on the HDDR-NdFeB showed an electron diffraction pattern that was almost the same as the pattern Diff 1 of the present MQP-B powders. Figure 4 shows magnified Diff 1 pattern, and Table 1 lists the analyzed result. The radii of the rings were calibrated by using strong diffraction spots of $Nd_2Fe_{14}B$. The diffraction rings in Table 1 are explained as a mixture of $Fe_{11}Zn_{40}$ and $NdZn_5$. There is a possibility that metallic zinc is also contained. The intensities of the diffraction rings sug-

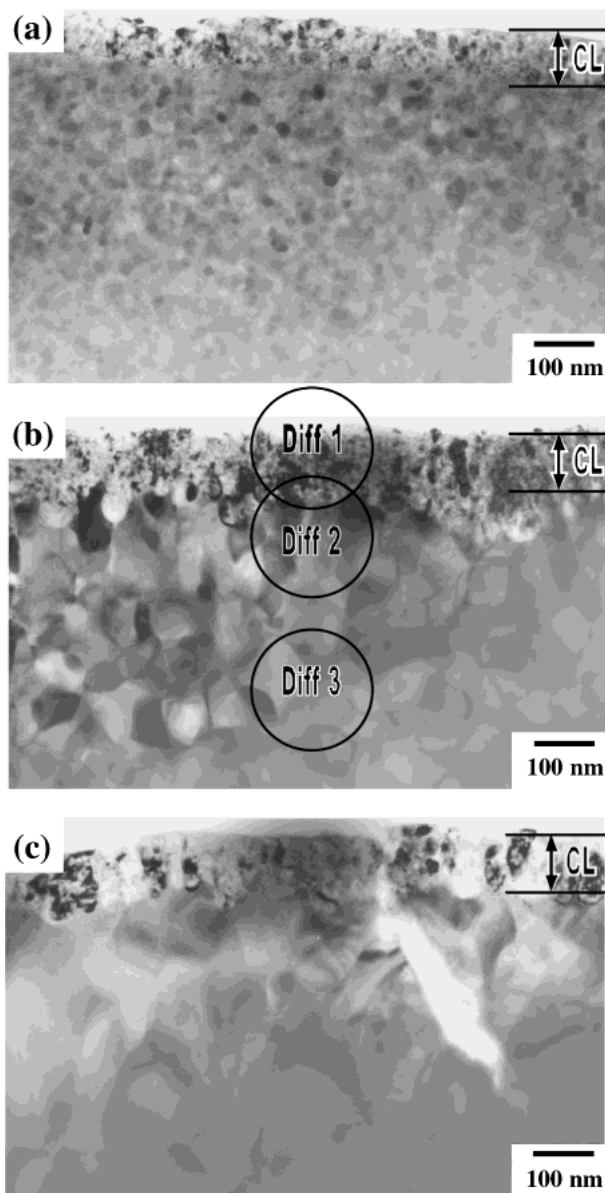Fig. 2   Microstructures of the different regions in Zn coated MQP-B powder treated at 623 K. (a) $Nd_2Fe_{14}B$ grain size ~ 30 nm, (b) $Nd_2Fe_{14}B$ grain size ~ 70 nm, (c) $Nd_2Fe_{14}B$ grain size ~ 100 nm. A thin coating layer (CL) has been formed on the surface of the powder.

gest that $Fe_{11}Zn_{40}$ phase exists as a main phase in the coating layer.

The microstructure of the coating layer can be seen clearly with high resolution transmission electron micrograph (HRTEM). Figure 5 shows a HRTEM image of a part of the coating layer. The marked lattice fringe spacing corresponds to (002) planes of $Nd_2Fe_{14}B$ grain. The whole area above the $Nd_2Fe_{14}B$ grain is full of small crystallites about 5–10 nm in diameter. These crystallites show different lattice-fringe-spacings from those of $Nd_2Fe_{14}B$. It is noted that there is no other layer found between the coating layer and the NdFeB grain region.

In case of NdFeB magnets, it is well known that the oxidation and corrosion usually occurs at the grain boundaries.[9, 10] For improving the corrosion resistance, it is necessary to modify the boundary. Recently, it was reported that the thermal stability of magnetic properties for HDDR-NdFeB powders is
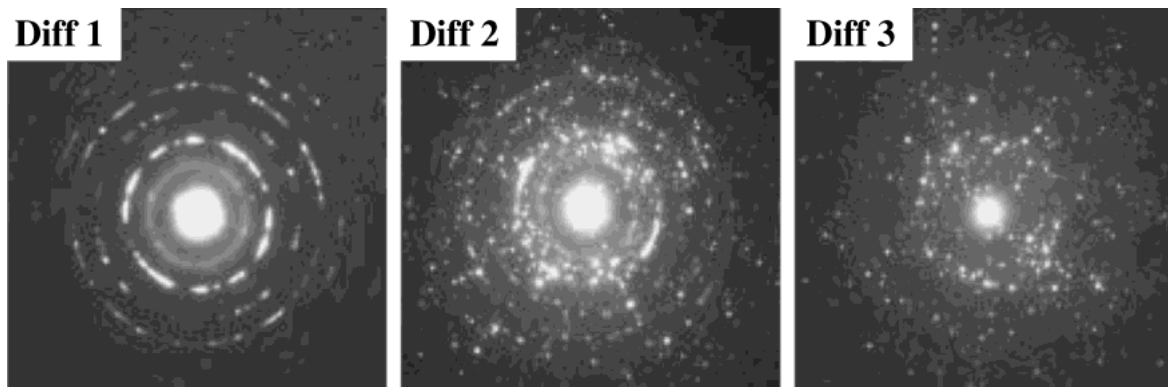
Fig. 3   Selected area electron diffraction (SAED) patterns taken from the marked areas in Fig. 2(b).
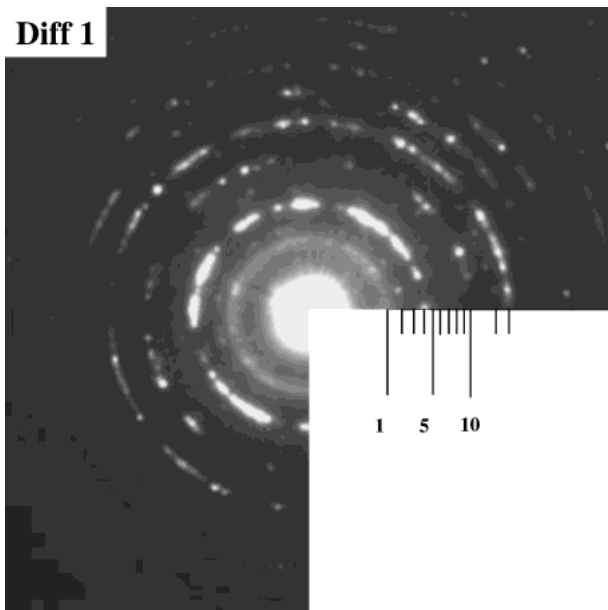

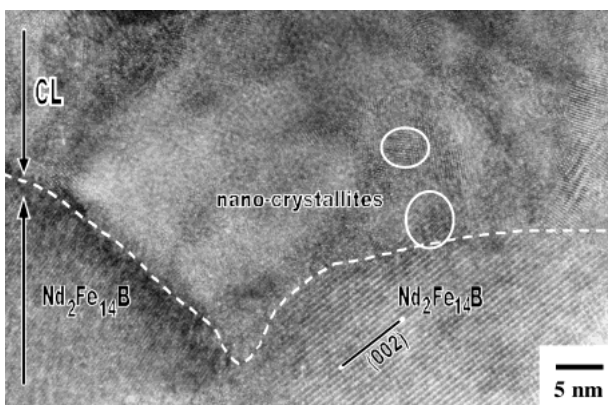Fig. 4   Magnification of Diff 1 in Fig. 3.

Fig. 5   High resolution transmission electron microscope (HRTEM) image of the coating layer formed on a MQP-B $Nd_2Fe_{14}B$ particle. CL: coating layer. Nano-crystallites about 5 nm have been formed in the coating layer.

Fig. 6   Microstructure of Zn coated MQP-B powder treated at 375°C. CL: coating layer. BL: boundary layer. It is noted that grains of $Nd_2Fe_{14}B$ are wetted with a boundary layer (BL).

significantly improved by the Zn vapor sorption treatment:[6] The magnetic flux loss, which increased to be 17% after an exposure in air at 392 K for 3.6 Ms, could be recovered to be a few percents by re-magnetization, while without the Zn vapor sorption treatment, the flux loss remained larg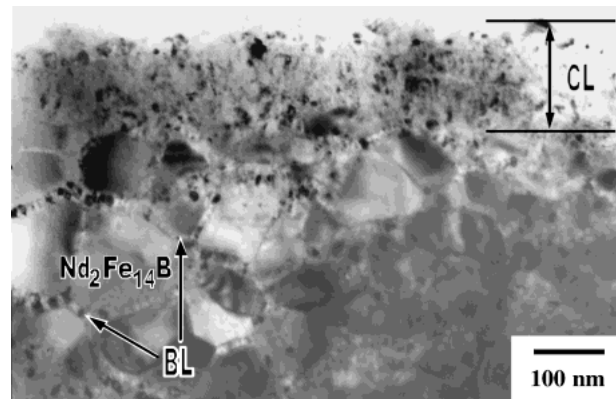er than 10%. The present workers[8] found that in HDDR-NdFeB powders after treatment at 623 K for 10.8 ks thin layers have been formed additionally at $Nd_2Fe_{14}B$ grain boundaries in the rim region near the surface of the powders. The boundary layers have the same constituents as the coating layer formed on the surface. The formation of the coating layer and the boundary layers is thought to enhance the corrosion resistance and the thermal magnetic stability. However, the Zn vapor sorption treatment under the same condition could not form the boundary layer in the MQP-B powders.

3.3   Microstructure of MQP-B powders after Zn vapor sorption at 648 K

Further study was performed to examine a possibility to form the boundary layer in MQP-B powders. Figure 6 shows the microstructure of MQP-B powders after Zn vapor sorption treatment at 648 K for 10.8 ks. In this area, $Nd_2Fe_{14}B$ grains are about 100 nm in diameter. The coating layer is formed to be about 130 nm thick. It is noted that the boundary layers about 20 nm wide have been formed at the grain boundaries of $Nd_2Fe_{14}B$. The modified microstructure is very similar to that in case of the HDDR-NdFeB powders, and the treatment is then expected to lead to the improvement in thermal stability of magnetic properties. However, by the present condition of treatment, the boundary layer was not formed in the region of $Nd_2Fe_{14}B$ grains smaller than 100 nm. Further study is under progress to survey more suitable condition for Zn vapor sorption treatment.

Table 1　Analysis of the SAED pattern (Diff 1).

Measured values			$Fe_{11}Zn_{40}$ (32–478)			$NdZn_5$ (27–325)			Zn (4–831)		
No.	d	Int.	d	I/I_0	hkl	d	I/I_0	hkl	d	I/I_0	hkl
1	3.00	s	2.998	10	442, 600						
			2.845	10	620						
			2.742	10	533						
						2.695	20	110			
2	2.62	s	2.598	30	444						
			2.519	30	711, 551						
			2.493	10	640				2.473	53	002
			2.404	60	642						
			2.343	60	553, 731	2.322	100	200	2.308	40	100
3	2.28	w				2.273	100	111			
			2.197	60	733						
			2.183	80	820, 644						
			2.120	100	660, 882	2.127	40	002			
									2.091	100	101
			2.078	80	751, 555						
4	2.06	ss	2.064	40	662						
						2.023	60	201			
			1.974	40	911, 753						
			1.962	30	842						
			1.918	30	664	1.919	20	102			
			1.887	30	931						
5	1.82	w	1.836	30	844						
			1.808	10	771, 933						
6	1.74	w	1.764	20	1020, 862						
7	1.70	vw	1.731	20	1022, 666						
									1.687	28	102
						1.648	10	112			
8	1.62	vw				1.632	10	211			
						1.589	100	202			
						1.569	40	300			
9	1.49	m									
10	1.46	s				1.451	20	301			
						1.404	40	003			
			1.377	10	933, 1155						
			1.356	10	1244	1.362	40	103			
			1.344	10	1331	1.339	40	220	1.342	25	108
			1.326	10	1262				1.332	21	110
			1.315	20	1333, 995						
			1.298	20	888	1.301	60	310			
11	1.29	m	1.285	10	1351, 1175	1.293	100	221			
			1.272	40	1420						
			1.262	30	1191, 1353	1.265	60	302			
						1.255	40	113			
			1.224	40	1442	1.238	20	311			
			1.215	10	1371, 1355	1.203	60	203			
12	1.18	ss	1.191	30	1444, 1088				1.1729	23	112
			1.153	30	1533	1.165	100	400			

Weak diffraction lines ($I/I_0 < 10$) have been omitted.

4.　Conclusions

The modification in the microstructure of MQP-B magnetic powders after Zn vapor sorption treatment has been clarified by TEM investigations. The thin coating layer about 100 nm formed continuously on the surface of MQP-B powders. The coating layer made of nano-crystallites is responsible for the improvement in the thermal magnetic stability of MQP-B powders after Zn vapor sorption. In addition, it is suggested that a more effective modification in microstructure with the boundary layers in rim region of the powders similar to Zn coated HDDR-NdFeB powders can be obtained by an appreciative condition for Zn vapor sorption treatment.

Acknowledgements

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